Silanation of Silica Surfaces. A New Method of Constructing Pure or Mixed Monolayers

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We present a quantitative study of different parameters of the silanation reaction (grafting of long aliphatic chains on silica surfaces via trichlorosilane group). Some of them, such as temperature or water traces, are shown to be particularly crucial. A mechanism for the reaction, completing the one previously reported, is proposed and optimal experimental conditions to perform high-quality monolayers of long aliphatic chains are deduced. Characterizations were performed with different techniques including X-ray reflectivity experiments and contact angle measurements. Results are consistent with well organized layers in which the chains are densely packed completely extended perpendicular to the surface. In the case of mixtures, the layer comportment reflects the concentration of each species in solution; there does not seem to be any segregation.

Introduction

Recently, a new way of constructing monolayers made of long aliphatic chains has emerged giving a powerful alternative to the Langmuir–Blodgett technique (LB monolayers).[1] In this technique, the resulting monolayer is chemically anchored to the surface, while LB monolayers are physically linked to it. Thus, these self-assembled monolayers (SA monolayers) are supposed to be stronger and more resistant than their LB counterparts. Of course, the more narrow range of substrates available for SA monolayers and the difficulty of constructing multilayers still allow a great deal of interest in LB layers.

SA monolayers had been successfully constructed on gold via a thiol group[2,3] and on silica via a trichlorosilane group.[4] This last category seemed very attractive on the one hand because of the large number of silica-like substrates (glass, metallic oxides, ...) and on the other hand because of the low roughness that can be achieved on some microelectronic silicon wafers covered with native silica. Treating such substrates with SA monolayers enables one to control hydrophilicity with no roughness effect. Sagiv and co-workers were the first to perform this type of grafting on plane surfaces,[5] a method previously used on beads in high-performance liquid chromatography to produce stationary phases.[6,7] However, one soon realizes that the chemical reaction, called silanation reaction, of grafting trichlorosilanes is not a trivial one. Reproducibility problems often arise due to the high number of relevant parameters.

The commonly assumed mechanism in these reactions stands in three distinct phases[5] (Figure 1). First, the aliphatic chains are strongly attracted to the clean silica surface via the trichlorosilane group, which acts like the polar head of an amphiphilic molecule. Like any oxide, silica surface is hydrated:[8] surface groups are silanols and silica substrates are covered with a water film (one or several layers thick). The trichlorosilane groups are then hydrolyzed when they get close enough to the surface (Figure 1). Chains are then bonded via hydrogen bonds to the surface silanols and to their close neighbors (Figure 1). This (unstable) situation is followed by water elim-

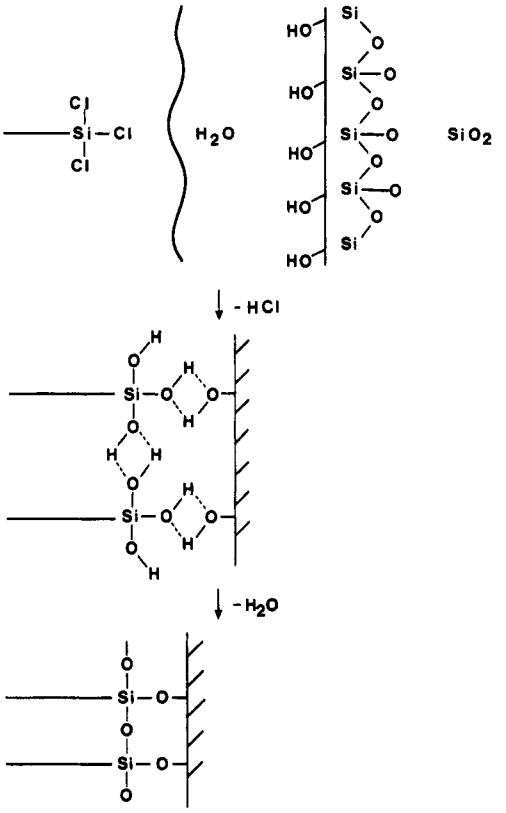

Figure 1. Schematic representation of the commonly assumed mechanism of the silanation reaction. The physisorption of the trichlorosilane molecules is followed by their hydrolysis and, finally, by water elimination, leading to a chemically anchored monolayer.

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ination leading to a network in which each chain is linked to the surface and to the other chains. This exceptional property gives very stable and well-oriented layers.[9] However this supposed mechanism is still hypothetical since only few systematic experiments have been performed in order to probe it. Moreover, a recent observation by Finklea et al.[10] showed that at least partial monolayers could be performed on gold, an oxide-free surface. Their conclusions was that the SA layer is grafted on the adsorbed water film on the gold substrate. For that reason and because of other concordant observations,[9,11] we felt that it was important to investigate the exact influence of water even in small quantities.

Temperature is also obviously an important parameter since it can affect the rate of reaction itself as well as the solubility parameter of the trichlorosilane molecules in the solvent. Finally, chain length as well as the presence of a terminal group can have a drastic influence on the surface quality and composition at the end of the reaction.[12]

The influence and importance of these parameters had been checked and we have deduced the optimal conditions for grafting monolayers made up with one or several molecules ("pure" or "mixed" monolayers).

Experimental Section

Formation of Monolayers. Monolayers were performed on silicon wafers (Siltronix, France). Trichlorosilanes were octadecyltrichlorosilane (OTS, $CH_3(CH_2)_{17}SiCl_3$) (this is the most common trichlorosilane available, it has been widely used and was our reference product), tetradecyltrichlorosilane (TTS, $CH_3(CH_2)_{13}SiCl_3$), and unsaturated TTS (u-TTS, $CH_2{=}CH(CH_2)_{12}SiCl_3$). OTS and u-TTS were obtained from Petrarch. TTS had been synthesized with a Grignard type reaction (see Appendix). All the silanation reactions were performed in a glovebox filled with dry nitrogen in order to minimize the amount of water traces in the surrounding atmosphere.

Wafers were first cleaned for 1–4 h by irradiation with UV light (λ = 185 nm and λ = 254 nm) in an oxygen flow.[13] This technique had been proved to efficiently oxidize any organic contaminant without altering surface roughness.[14,15] Wafers were then exposed to a water-saturated nitrogen flow for 1 min (this, which has been proved to be necessary to the reaction, is believed to restore the water film which would have been potentially removed by the cleaning procedure) and introduced into the glovebox.

Reaction occurred in a glass beaker containing the silanation solution. The beaker itself is placed in an ultrasonic bath in which the contact liquid is dodecane maintained at a fixed temperature. When we did not use ultrasonic waves, we have noticed a stronger heterogeneity of the surface. They are thus thought to prevent polymerization of the free trichlorosilanes near the surface during the reaction and to remove the physisorbed material, which may hinder the chemical reaction itself.

Solutions were prepared prior to reactions: for OTS, 70 cm^3 of hexadecane (HD), 10 cm^3 of CCl_4, 2 cm^3 of water-saturated chlorinated solvents prepared by decanting two volumes of $CHCl_3$ and three volumes of CCl_4 under water drops overnight [$(CHCl_3/CCl_4)_{H_2O}$], and 200 μL of OTS (6.2×10^{-3} M); for TTS and u-TTS, 70 cm^3 of HD, 20 cm^3 of CCl_4, 2 cm^3 of $(CHCl_3/CCl_4)_{H_2O}$, and 200 μL of TTS or u-TTS or mixtures (5.5×10^{-3} M).

All solvents were obtained from SDS (France) (anhydrous grades) and used as received, except HD which was filtered. OTS silanations were performed at 18 °C for 2 min and TTS or u-TTS silanations were performed at 10 °C for 6 min. After reaction, treated wafers were thoroughly rinsed with anhydrous chloroform. From that point, they were stored in individual boxes. Their qualities remained unchanged for months.

Characterization of the Monolayers. To check the completion of the reaction, XPS experiments were performed on the monolayers giving a chemical analysis of the surface. Contact angle experiments as well as X-ray reflectivity measurements were then performed to investigate the macroscopic and microscopic characteristics of the layers.

Contact angles were measured by using a previously described method,[16] which uses the geometrical characteristics of a parallel beam after its reflection on a drop. This device, giving a global image of the triple line, allows an accurate determination (±0.5°) in the range 5–40°. The measurements were performed by using alkanes (Fluka, puriss., used as received) and triply distilled water. For this latter measurement, the drop was lighted from behind and its image projected on a screen.

Using a series of homologous *n*-alkanes in a Zisman plot,[17] one can extrapolate the critical gamma (γ_c) of the surface (e.g. the surface tension of an hypothetical liquid which would be exactly at the wetting–nonwetting frontier). Unless otherwise specified, reported contact angles were advancing contact angles. Hysteresis had been measured and was defined as $\Delta = \cos\theta_r - \cos\theta_a$ (where θ_a and θ_r are respectively the advancing and receding contact angles).

X-ray reflectivity experiments were performed on a 4-circle diffractometer.[18] The source is a conventional fine-focus copper-tube source. This technique has already been described;[18-20] it consists of analyzing the reflectivity curve (reflectivity vs incidence angle) in terms of Fresnel's law.[21] Equal thickness interferences occur in the layer, leading to oscillations in the reflectivity curve. The angular position of the first minimum gives the thickness, its contrast yields to the electronic density of the layer. Finally, the roughness of the interface is given by a more global fit of the curve. These three parameters are thus independently determined, which makes this technique particularly valuable.

Results

When prepared by the described procedure, wafers treated with OTS or TTS emerged dry from the silanation solution. For OTS, TTS, and u-TTS treated wafers, no chlorine element could be detected on XPS spectra indicating a completion of the chemical reaction.

X-ray reflectivity experiments showed a dense layer of thickness 22 ± 1 Å for OTS (see Figure 2) and 18 ± 1 Å for TTS or u-TTS, values in good agreement with the all extended aliphatic chain length. Roughness of the air–layer interface is about 3 Å, slightly less than that of the bare substrate (ca. 5 Å). A Zisman plot of OTS layers gave γ_c = 20.5 ± 0.5 dyn/cm (see Figure 3) and water contact angles were measured at 108 ± 2°. These results are in good agreement with those previously reported on similar layers.[19,22,23]

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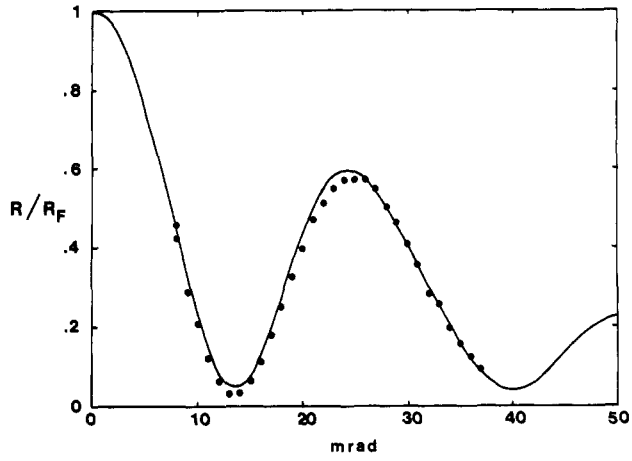

Figure 2. X-ray reflected intensity at different incidence angles for an OTS monolayer. The reflectivity had been divided by the Fresnel reflectivity. The dots are the experimental points. The solid line is the fit yielding to the geometrical characteristics of the monolayer.

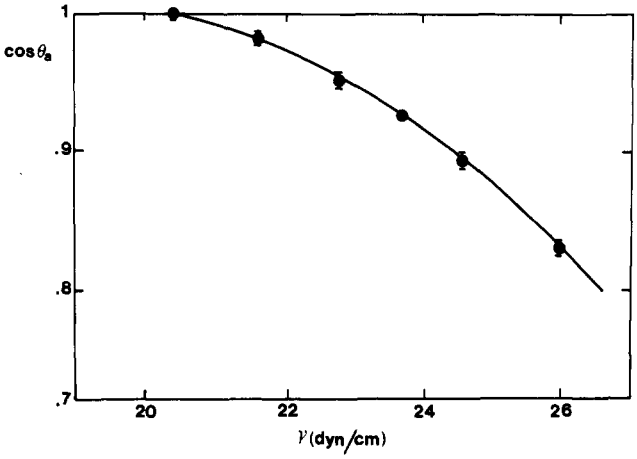

Figure 3. Zisman plot of an OTS monolayer. As is often observed, the points follow a linear comportment only in a very crude approximation. A parabolic model (solid line) yields $\gamma_c \cong 20.5 \pm 0.5$ dyn/cm.

It should be emphasized however that a direct comparison of absolute contact angles (for example as they can be measured in different laboratories) is very tentative: first, the method we use,[16] when the liquid is an alkane, despite its obvious advantages (an estimation of the distortion of the triple line and a measurement of the contact angle all around the drop instead of two points with a conventional goniometer), is not widely used and there is some evidence that measurements made with the more conventional methods tend to overestimate contact angles compared to our values.[24] Moreover, a contact angle is very dependent of the quality of liquid used (for example, we have sometimes noted discrepancies of several degrees according to the quality of water used for measurements). We have performed a direct comparison of contact angles measured with our device on our OTS-silanated wafers and on similarly treated surfaces (silicon wafers and mica) exhibiting among the highest contact angles ever reported in the literature.[24] Very close values were obtained, confirming the good quality of the surfaces obtained when following the experimental procedure described above. In the following, all contact angle mesurements were performed using always the same liquid (same quality or even

(24) Thanks to Professor J. Sagiv and Dr. R. Maoz who have provided us with their samples and have thus allow direct comparative experiments.

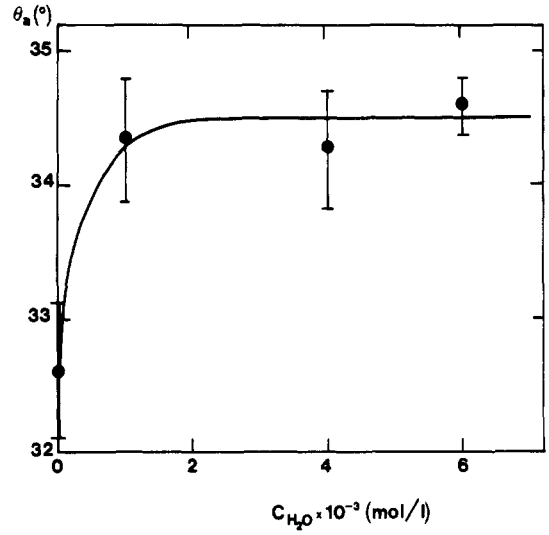

Figure 4. Influence of the water concentration in solution on the silanation reaction. θ_a is the advancing dodecane contact angle on a silanated wafer; C_{H_2O} is the initial water concentration. Water is necessary in small quantities. Experimental conditions were 18 °C and 2 min reaction time.

same bottle when possible) and are only meant to be relative from one monolayer to another.

The difference of experimental procedures for silanation with TTS is characteristic of the difficulty of grafting shorter chains, a fact already observed.[25]

Water traces that are introduced in the mixture through the water-saturated chlorinated solvents proved to be essential to the silanation reaction (see Figure 4). The water concentration in the silanation solution can be calculated to be about 6×10^{-3} M.[26] Temperature also is an essential parameter. A variation of a few degrees of the silanation solution temperature can have a dramatic effect on the layer hydrophobicity as well as its quality (see Figure 5).

Wafers treated with u-TTS or with a mixture u-TTS + TTS showed the same "geometrical" characteristics (thickness, density, roughness) as TTS layers. However, dodecane is in total wetting on u-TTS treated wafers compared to a contact angle of 34° after a TTS treatment.

This behavior may be indicative of the higher polarizability of the terminal group on the surface (ethylene for u-TTS compared to methyl for TTS). However, some authors have measured finite contact angles for dodecane on comparable layers.[27] As a matter of fact, we do not have definite evidence of the terminal functionalities of the chains after the grafting of u-TTS; the vinyl groups exposed to the surface are very reactive and can be easily modified: chlorination in the reaction bath, oxidation in the atmosphere, polymerization, and so on. A number of these possibilities can be easily checked; the absence of the chlorine element with XPS experiments and very high water contact angles on u-TTS treated wafers (~100°) are not compatible with either chlorinated or oxidized substrates. Moreover, we have successfully performed a bromination of these u-TTS treated wafers, another indication of the presence of double bonds. However, some other kind of alteration such as partial polymerization may have occured. If this happened, this surface modification must be very fast (in the reaction bath or right

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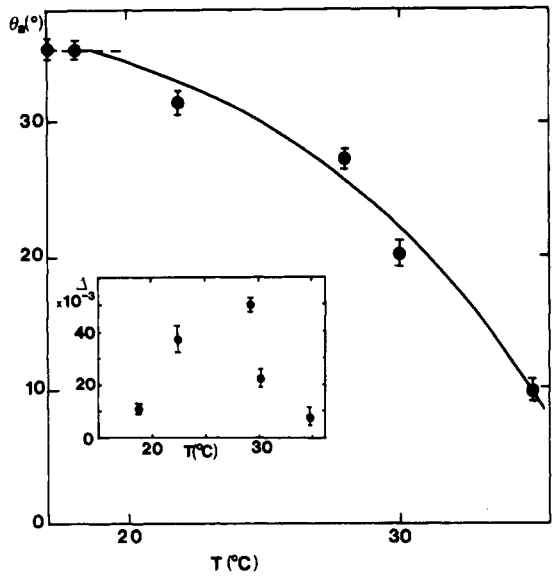

Figure 5. Influence of temperature on the silanation reaction. Note the dramatic effect of a small variation in temperature on the advancing contact angle of dodecane. In the insert, effect of temperature on the hysteresis. High temperatures can yield very high hysteresis values, a sign of heterogeneity of the monolayer. Experimental conditions were $C_{H_2O} = 6 \times 10^{-8}$ M and 2 min reaction time.

after reaction) since no evolution of the surfaces can be detected even after several months; it would also be very reproducible. Considering the surface energy point of view, this would not affect the generality of what is presented in this study.

Mixed monolayers have been realized by using different relative concentrations of TTS and u-TTS, the total concentration being kept constant. On such layers, dodecane comportment is intermediary between that on each of the "pure" layers. The cosine of its contact angle versus β, concentration of u-TTS in solution, showed a linear comportment in the partial wetting region following nicely the so-called Cassie's law[28] (see Figure 6a). Hysteresis was about constant at any concentration (see Figure 6b). We inferred from these observations that any γ_c intermediate between values of single component layers can be obtained simply by adjusting the relative concentrations of TTS and u-TTS in the silanation solution.

Discussion

All the data presented are consistent with close packed monolayers; chains are extended perpendicular to the surface in an all-trans configuration, exposing their terminal group.

The fact that the roughness is lower for silanated wafers is compatible with a vision in which the layer is not linked to the surface by all the individual molecules but, rather, forms a "net" where molecules are linked to each other; this net would be bonded to the surface by only a few bonds. The nature of these bonds, i.e. the way this net is linked to the surface, is still unclear but the necessity of water traces for the reaction to occur may be a clue of a water layer adsorbed on the surface. If this film is strongly linked to the surface by hydrogen bonds, the reaction can occur on it instead of occurring on the silanol groups (Figure 7). Finklea et al.[10] explained similarly their silanations on gold in partially hydrated conditions. However, in our experiments, the much stronger attractivity of silica for water yields to layers of better quality.

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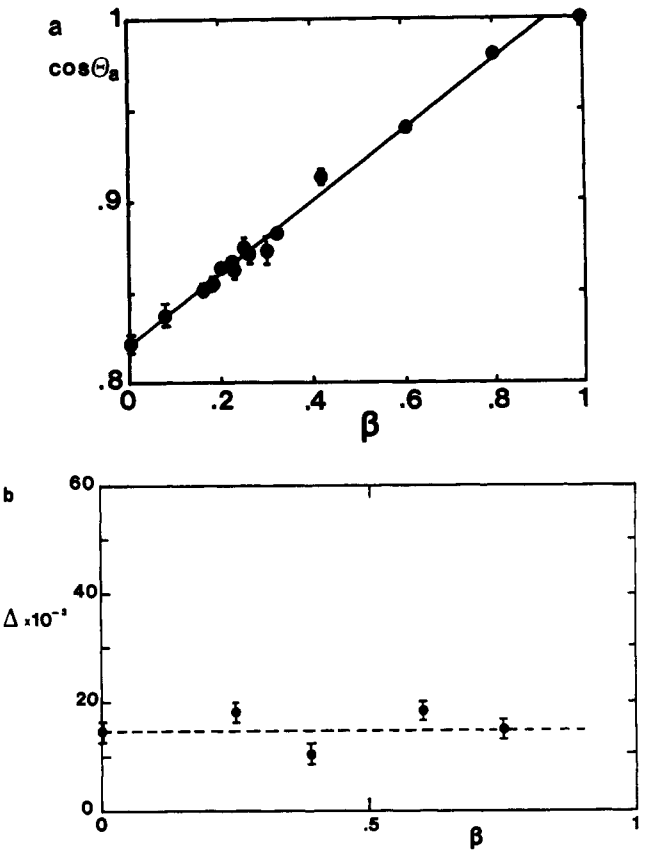

Figure 6. (a) Cosine of the dodecane contact angle at different u-TTS concentrations in solution. The linear comportment observed can be interpreted in terms of Cassie's law (solid line). The dots are the experimental points. Experimental conditions are described in text. (b) Hysteresis of the dodecane contact angle for different u-TTS concentrations in solution. The scale is the same as in Figure 5, insert. Note the very stable (and very low) value indicating a homogeneous layer (see text for details).

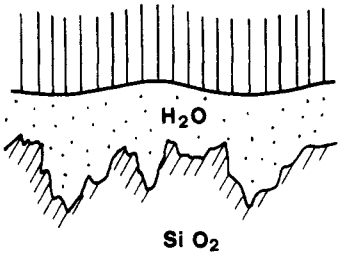

Figure 7. Tentative schematic disposition of the silane molecules at the end of the grafting procedure. A water film is intercalated between the molecules (the "net") and the substrate.

We can now attempt to complete the usually admitted mechanism: The first step would be a strong and quick adsorption of a water film, which would be followed by the silane physisorption on this film. Then, the chemical reaction itself would take place on it, linking the silanes together and anchoring the net to the water film.

Although it is important in the grafting, water is often dissembled because of its uncontrolled quantity in most of the usual solvents. We have shown that a small amount of water is necessary; of course, too much water should be avoided to prevent a polymerization of the trichlorosilane in the silanation solution.[9]

Temperature of the reactional medium had been seen to be another important parameter (Figure 5). Low temperatures favor grafting, which seems paradoxal at first sight (the chemical reaction being slowed down). This effect can be interpreted by the fact that a low temper-

ature decreases the solubility of either water or the silane molecules increasing accordingly the kinetics of the physisorption step. Moreover, when shorter chains are used (TTS instead of OTS), a lower temperature becomes necessary, meaning that temperature is affecting the silane physisorption step; high temperatures reduce the amphiphilic behavior of these molecules. This effect is enhanced when using short chains.

Thus, optimal experimental conditions result from a balance between temperature and reaction time but in a nontrivial way: a lower temperature does not necessarily imply a longer reaction time. For example, an OTS monolayer achieves its optimal quality in 2 min at 18 °C while even a 24-h reaction time did not lead to a satisfactory result at 30 °C.

For the two molecules we used, layer quality is chain length independent; when grafting is performed under optimal conditions, OTS and TTS monolayers exhibit the same contact angles with dodecane, hexadecane, and water, and their geometrical characteristics are consistent.

Finally, we have shown that when making monolayers from two components differing only slightly from their terminal group, the contact angle of a reference nonpolar liquid follows nicely a linear behavior vs the composition of one of the constituents.

Cassie,[28] considering a surface made of patches of components 1 and 2, proposed a linear law

$$\cos\theta = \beta\cos\theta_1 + (1-\beta)\cos\theta_2$$

where θ, θ_1, and θ_2 are the equilibrium contact angles of the liquid on respectively the mixed and each single component monolayer and β is the concentration of compound 1 on the surface. However, it was then assumed that the considered liquid was in partial wetting on surface 1 as well as on surface 2, which is not the case here (dodecane is in total wetting on pure u-TTS surfaces).

The same remark applies to the more recent law inferred by Israelachvili and McGee[29]

$$(1+\cos\theta)^2 = \beta(1+\cos\theta_1)^2 + (1-\beta)(1+\cos\theta_2)^2$$

if there is no segregation.[30]

However, the linear comportment we observe can be interpreted as a generalization of these laws.

The fact that the hysteresis of the dodecane contact angle remains constant when varying β (Figure 6b) is probably due to a nonsegregated monolayer;[29] however we cannot completely rule out the possibility of a layer made of patches of TTS and u-TTS. If these domains exist, they must be small (ca. <100 nm) as proved by the extensive study of Schwartz and Garoff.[31]

Conclusion

We have systematically studied a number of relevant parameters of the silanation reaction. Among them, water traces and temperature were shown to be crucial and have to be controlled during the reaction process. When using the optimal experimental conditions described, one can obtain high-quality monolayers. The proposed technique is particularly reliable and fast. A more detailed mechanism is proposed to explain our observations.

Finally, we have shown that mixed monolayers can be built enabling one to obtain any critical surface tension between the two single-component surface values. There seems to be no segregation between the two species.

The faculty of being able to perform layers of adjustable surface energy can find a large number of applications including wetting,[32] adhesion, or adsorption.

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Appendix. Synthesis of TTS

This synthesis is very similar to the one described by Wasserman et al.[11,33] Reagents were purchased from Aldrich and solvents from S.D.S. (France) (anhydrous quality).

Prior to reaction, solvents were dried by reflux with CaH_2 during several hours and then distilled. The glassware was allowed to stay at least overnight at 110 °C.

Magnesium (5 g, 5.1 equiv) and dry THF (10 mL) were placed in a dry tricol equipped with a water-cooled condenser and an addition funnel containing the bromide reagent. The mixture was heated at reflux and reaction was initiated by ethane dibromide (2 drops). Tetradecyl bromide (10 g in 90 mL of dry THF) was then added dropwise and the mixture was allowed to react for 8 h. The solution was then cooled down to about 30 °C, a temperature at which it is still liquid.

Silicon tetrachloride (10.2 mL, 2.5 equiv) and 100 mL of dry ether were placed in another dry tricol equipped with a water-cooled condenser and a rubber septum. The warm Grignard reagent was added through a cannula and the mixture was allowed to react for 10 h. The solution, which now contains a white precipitate, is cooled down at room temperature and brought to a boil in a distillation apparatus to remove the solvents and the excess $SiCl_4$. The remaining solid is then triturated with dry hexane (2 × 20 mL) and centrifuged.

The liquid fraction is distilled by using a short path distillation apparatus. Hexane is removed at ambient pressure. The remaining liquid is vacuum distilled. The second fraction (138–140 °C, 0.2 mmHg) is a clear oil. IR and NMR spectra (^1H and ^{29}Si) showed a structure compatible with TTS. Yield was about 40%.

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